

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3207

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SUMMARY

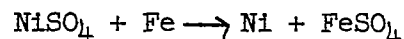
An investigation was made of the effects of (a) the firing time and (b) the weight of nickel deposited from the nickel-dip solution on the adherence developed by a cobalt-free and a cobalt-bearing ground-coat enamel on both enameling iron and a titanium-bearing low-carbon steel. At 1550° F it was found that the maximum benefit from the nickel on the measured adherence index occurred at 2-minute firing. The effect of the nickel, however, dropped markedly with longer firing times. It was also found that there was an optimum nickel deposit for maximum adherence. This optimum varied from 50 to about 120 milligrams per square foot, depending on the type of cleaning used and the type of enamel applied.

It was found that the nickel dip reduced the tendency toward fish-scaling. Furthermore, there appeared to be a relation between fishscaling resistance and good adherence; no specimen with an adherence index of 70 or over showed fishscaling tendencies.

Metallographic studies of the interface of coated specimens showed that nickel dipping of the steel prior to enameling brought about a surface roughening during the firing operation. A relation was noted between the degree of roughening and the measured adherence index. The roughening of the steel surface was ascribed to galvanic corrosion.

INTRODUCTION

The nickel dip, or nickel flash, is used extensively in the porcelain-enameling industry to improve coating quality. The process consists of immersing the part to be coated for about 5 minutes in a weak aqueous solution of nickel salts at 1500 to 1700 F and at a pH adjusted usually to 3.0. The part is immersed in the nickel-dip solution following the cleaning operations but prior to the application of the coating. During the process a thin film of metallic nickel is plated on the steel by a galvanic replacement reaction. The reaction may be written as follows:



The presence of a nickel film on the steel is reported (a) to insure adherence of the coating to the metal over a wider range of time and temperature for the firing process and (b) to reduce the incidence of delayed fishscales¹ and copperheads².

Several investigators have theorized that the thin layer of nickel deposited from the nickel dip retards oxidation of the steel during the firing operation (refs. 1 and 2). Too much oxide at the interface is supposedly detrimental to development of adherence. Thus, by inhibiting the formation of oxide, especially during the early part of the firing cycle, the nickel dip is believed to improve the bond between the coating and the iron base.

Such a suggested mechanism does not conform to the galvanic corrosion theory as outlined in an earlier paper (ref. 3). This theory postulates that good adherence results from the roughening imposed on the steel surface by a molten enamel containing either cobalt or nickel ions. According to this theory, adherence is caused mostly by mechanical gripping. If the nickel dip, on the other hand, produces adherence by some mechanism other than by a surface-roughening action, then the responsible mechanism should be isolated and studied if a complete understanding of ceramic-to-metal adherence is to be achieved.

The purposes of the present investigation were (1) to determine quantitatively the effects of the nickel dip on the development of adherence and fishscaling tendencies of a typical ground-coat enamel and (2) to determine the most probable mechanism through which the presence of the nickel aids in development of bond. The present investigation represents one phase of a broad study of the adherence of ceramics to metals which is currently being conducted at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

MATERIALS

Two steels were included in the investigation: Enameling iron (steel A) and titanium-stabilized low-carbon steel (steel B). Representative analyses are given in table 1.

¹Fishscales are localized fractures of the coating commonly ascribed to excessive hydrogen pressure at the interface. When the fractures occur several days or even several months after the coating has been applied, the defect is referred to as delayed fishscales.

²Copperheads are reddish-brown spots that are sometimes present on ground-coat enamels after firing. They are commonly ascribed to small blisters in the coating layer that do not heal completely before the firing is terminated.

Table 2 gives the mill batches for the two ground coats. The frit used was selected from an earlier study (ref. 4) as being suitable for the preparation of a single-frit enamel ground coat. The frits used in the E-1 and E-3 enamels are identical except that the one used in E-3 contained 0.4 percent by weight of cobalt oxide, whereas the other contained none. The batch and computed oxide compositions for frit 109-0 used in coating E-1 are given in table 3.

PREPARATION OF SPECIMENS

The specimens needed in the investigation were prepared by shearing 4- by 4-inch blanks from 18-gage sheets, 600 specimens being required.

Three specimen pretreatments were used: A sulfuric-acid pickle, a nitric-acid pickle, and sandblasting. Table 4 gives the concentrations, bath temperatures, and immersion times for the two pickling solutions. The specimens were degreased prior to pickling in a boiling solution of a commercial alkaline cleaner. Sandblasting, when used, was done at an air pressure of 80 pounds per square inch with a silica sand that was sized so as to pass a No. 20 U. S. Standard sieve and be retained on a No. 100.

The concentration of the nickel-dip solution, the operating temperature, and the standard immersion time are given in table 4. After their removal from the nickel-dip solution all specimens were rinsed in a sodium-cyanide neutralizer, after which they were dried at 212° F.

Both the E-1 and E-3 coatings were applied by dipping. The consistency of the slip (coating suspension) was adjusted so as to give a thickness of 4 to 6 mils on the fired specimens. All specimens were fired in an electrically heated box furnace, having inside dimensions of 17 by 13 by 35 inches.

TEST PROCEDURES

All adherence measurements were obtained in accordance with the tentative standard adherence test of the Porcelain Enamel Institute (ref. 5). This test evaluates the degree of adherence of a porcelain enamel to metal in terms of the amount of metal exposed after a standard deformation treatment, expressed as a percentage of the total deformed area. Although there is no standard classification of adherence indices, values below 50 may be considered as poor adherence, 50 to 75 as fair, 75 to 90 as good, and 90 or above as excellent.

The weight of nickel on the metal surface was determined by a modification of the method of Ikenberry and Canfield (ref. 6)³. In all cases nickel determinations were made on duplicate specimens, the average for the two being the reported value.

RESULTS AND DISCUSSION

Effect of Nickel Dip on Adherence

Table 5 gives the adherence data for coating E-1 applied to the two steels after various surface pretreatments and after 5 different firing periods at 1,550° F. In each case the nickel dip improved the adherence, the improvement being greater for steel B than for steel A. The best adherence for the nickel-dipped specimens was obtained after the 2-minute firing time, the adherence index falling off with longer firing. This is shown graphically in figure 1, which is a plot of the firing times against the average adherence values for the three surface pretreatments.

Table 6 and figure 2 give the same type of data for the cobalt-bearing ground coat E-3. It will be noted that the maximum effect of nickel dip on adherence is observed at short firing times; at longer firing times the effect of the nickel is largely obscured by the adherence-promoting effect of the cobalt oxide in the enamel.

Figures 3 and 4 show the effect of the amount (weight) of the nickel deposit on the adherence index for coatings E-1 and E-3, respectively, when fired for 5 minutes at 1,500° F on steel B. In each case there appears to be an optimum weight of nickel for best adherence, it being somewhat lower for pickled specimens than for sandblasted. The optimum obtained for pickled specimens occurs at 50 milligrams per square foot for coating E-3 and 80 milligrams per square foot for E-1. These values agree well with the values given by Wainer and Baldwin (ref. 1) for both zircon and antimony enamels applied directly to titanium-bearing steel. These authors reported an optimum of 50 milligrams per square foot for the zircon enamel and 80 milligrams per square foot for the enamel containing antimony.

³The test procedure of Ikenberry and Canfield was modified so as to insure against possible errors resulting from the presence of finely divided ferric hydroxide in the filtered solution. In the modified procedure, as devised by Dr. H. B. Kirkpatrick of the Enamelled Metals Section of the National Bureau of Standards, interference from iron in the solution was eliminated by complexing the iron with citrate ions.

Effect of Nickel Dip on Fishscaling

Several investigators have recommended the use of the nickel dip as a deterrent to fishscaling (refs. 7, 8, and 9). In the present work, all specimens coated with ground coat E-3 were inspected 24 hours after firing for the presence of fishscaling. Only three specimen groups showed traces of fishscaling at the time of this inspection, these groups being so identified in table 6.

In an attempt to accelerate delayed fishscaling, all specimens were heated for 40 hours in air at 260° F. This treatment is in general agreement with that suggested by Derringer (discussion of ref. 10) except that a somewhat lower temperature was used in the present work.⁴ Table 6 shows that fishscaling was much more prevalent after this treatment. No further fishscaling occurred after 2 months' storage at room temperature and for this reason the treatment is believed to show promise as a test for delayed fishscaling. The treatment should not, however, be accepted as a sure indication of delayed fishscaling without further study.

The data in table 6 show that the nickel dip does not always prevent fishscaling. The type of steel is important, the titanium-stabilized metal (steel B) showing no fishscaling under any of the firing conditions or for any of the surface pretreatments. In the case of the enameling iron, fishscales did not appear on any specimen showing an adherence index greater than 70, but several specimen groups fired at 10 and 16 minutes did not fishscale although the adherence index in one case was as low as 53.9. The reason why specimens fired for longer times did not show fishscaling is believed to be associated with the presence of bubbles at the interface. Figure 5 shows the change in bubble structure with increasing firing time. The bubbles in contact with the interface in figure 5(c) are of a type shown previously (ref. 11) to be caused by the rapid evolution of hydrogen from the steel during fast cooling of the specimen. These bubbles apparently served as reservoirs for the hydrogen that diffused from the steel structure after the specimen had cooled. Fishscaling did not occur on any specimen where such bubbles were observed.

Table 5 shows the same type of data as table 6 except that in the case of the cobalt-free enamel (E-1) true fishscaling was not observed. Instead, "lifts" (ref. 12) appeared on the specimen immediately upon cooling and further aging either at room temperature or at 260° F had no effect except to enlarge and, in some cases, to fracture the lifted areas. It is interesting to note that those specimen groups that showed fishscaling with the E-3 coating showed lifts when the E-1 ground coat was applied. This indicates that the same basic mechanism is responsible for both defects.

⁴Earlier work (ref. 9) indicated the possibility of hydrogen diffusing through the coating layer at the 400° F temperature suggested by Derringer; hence the lower temperature was selected.

Effect of Nickel Dip on Oxidation of Steel

Previous investigators have reported that the nickel dip retards oxidation of the steel (refs. 1 and 2). As a check on this earlier work, a few tests were made of the gain in weight of uncoated 4- by 4-inch specimens of both steel A and steel B after firing for 2 minutes at 1,550° F. The results of the tests, which are given in table 7, show that the nickel-dip treatment did, in fact, retard the oxidation of pickled specimens, the effect being greater for steel B than for steel A. The increase in adherence index from the nickel dip was also greater for steel B than for steel A. Table 5, for example, shows that in the case of coating E-1 fired 2 minutes at 1,550° F the nickel dip increased the adherence index of steel A pickled in sulfuric acid from 4.2 to 18.2 while in the case of steel B the increase was from 3.6 to 76.4. It should be pointed out, however, that sandblasting (see table 7) retarded oxide formation on the specimens to a much greater extent than the nickel dip; yet table 5 shows that sandblasting failed to increase the adherence index by a proportionate amount. Also, it was found that a heavy deposit of nickel obtained by electroless deposition (ref. 13), which would be expected to reduce oxidation to a much greater extent than the nickel dip, actually prevented adherence of the enamel layer. Because of these two observations it seems improbable that the principal mechanism through which the nickel dip improves adherence is by retarding the oxidation of the steel surface.

Nickel Remaining on Steel After Various Firing Treatments

An attempt was made to determine whether or not any of the deposited nickel is oxidized during firing and then dissolved in the enamel layer. A chemical determination for nickel on specimens of steel B was made prior to coating application, and a second determination made on a different area of the same specimens after coating E-1 was applied, fired, and later stripped from the metal by immersing the specimens for 5 minutes in molten sodium hydroxide held at 800° F. This treatment appeared to remove the enamel but, at the same time, left an iron-oxide-colored film on the surface. Table 8, which gives the results for specimens fired for 4 minutes at 1,400°, 1,500°, and 1,600° F, shows no significant difference in the weight of nickel at the metal surface before and after firing.

Richmond, Kirkpatrick, and Harrison by use of radioactive nickel as a tracer also found that the nickel remained at or near the interface during the firing treatment (an unpublished paper). These same men found, however, that some of the radioactivity that remained at the specimen surface after deenameling in molten sodium hydroxide could be removed by a subsequent treatment with ammonium citrate. This treatment dissolved the aforementioned residual oxide-colored film from the specimen surface and, at the same time, dislodged an insoluble residue that settled to the bottom of the citrate solution. The citrate solution was not radioactive

but the residue was. Therefore, because of its insolubility in the citrate solution, the residue may well have consisted of tiny metallic particles, rich in nickel, that had become freed from the specimen surface during firing and ended up imbedded in the iron oxide-rich layer near the interface.

Effect of Nickel Dip on Appearance of Enamel-Metal Interface

Metallographic sections were prepared from a few of the nickel-dipped specimens that showed maximum changes in adherence index with increasing firing time at 1,550° F. These were compared with sections of specimens that had the same treatment except that they had not been nickel-dipped.

Figure 6 shows a series of these coating-metal interfaces for coating E-1 applied to pickled specimens of steel B. These photomicrographs show that the nickel dip produces a surface roughening that resembles the roughening observed when cobalt is present in the enamel. With increasing firing, however, the roughness diminishes and the adherence of the coating decreases accordingly.

PROBABLE MECHANISM THROUGH WHICH NICKEL DIP FUNCTIONS

Recent work in the NBS laboratory (ref. 14) showed that there was a good correlation between the roughness of the interface and the adherence of porcelain enamel to steel. A second paper (ref. 3) discussed the galvanic-corrosion theory and showed how galvanic attack could cause the type of surface roughening observed when enamels containing either cobalt or nickel are applied to low-carbon steel. This galvanic-corrosion theory, which was expounded earlier by Dietzel (ref. 15), pictures the cobalt as plating out selectively on the iron surface from the molten enamel electrolyte by a galvanic replacement reaction⁵. The precipitated cobalt in contact with the iron base forms a couple, or short-circuited local cell, in which iron is the anode and cobalt the cathode. The current flows from the iron through the melt (molten coating material) to the cobalt and back to the iron. During firing, these couples continue to function for an appreciable time because there is an abundance of iron on the anode side, and diffusing atmospheric oxygen has a depolarizing action on the cathode side. The result is that iron from the anodic areas goes continually into solution, the surface becomes roughened, and the coating anchors itself into the undercut surfaces.

⁵That cobalt does in fact plate out on the iron during the firing operation was shown by radioactive tracer techniques (ref. 16).

From the evidence obtained in the present investigation, it appears that a nickel deposit, when applied to a steel surface by a galvanic replacement reaction, improves the adherence in much the same way. The nickel apparently deposits from the aqueous solutions selectively on cathodic areas of the steel surface, thus forming local galvanic cells that begin to function immediately after the enamel electrolyte fuses and wets the metal surface. These cells are not reformed, however, as is believed to be the case when Co^{++} or Ni^{++} ions are present in the coating layer (ref. 3) and thus they become depleted as firing continues. The depletion is believed to result, for the most part, from dislodgment of those fragments of steel over which the nickel had originally plated. Galvanic corrosion would be expected to undercut these plated areas quite rapidly, thus freeing fragments of metal into the enamel layer. Detached particles of this type can be observed near the interface in microsections (see fig. 6) and, in addition, the presence of such metallic fragments was demonstrated by the radioactive tracer work. This same work indicated, however, that only a part of the nickel disappeared from the steel surface during firing. The nickel that remains might be expected to continue to favor galvanic corrosion and the accompanying surface roughening. The observation that such is not the case (see fig. 6) indicates that the nickel remaining on the steel loses its effectiveness, galvanicwise, as the firing continues. Diffusion of the nickel into the iron structure is a possible cause for this behavior. That such a diffusion does occur and that the amount of diffusion is a function of the severity of the firing treatment was ably demonstrated in a recent investigation by Patrick, Porst, and Spencer-Strong (ref. 17). The difference between adherence development when cobalt ions are present in the coating and when a galvanic nickel deposit is plated on the steel is well brought out in figure 7.

The galvanic-corrosion theory agrees well with the various observations made in the present study. It explains, in particular, why the surface of the nickel-dipped steel becomes roughened when a cobalt-free enamel is applied and fired, and it also offers an explanation for the decrease in adherence with increase in firing time. In addition, the galvanic-corrosion theory explains why an optimum nickel layer is necessary for maximum adherence development. If less than the optimum nickel is present, the anodic areas of the iron surface could be looked upon as being too large; the anodic current would be weak resulting in a shallow uniform corrosion of the exposed iron areas. If, on the other hand, too much nickel were applied the anodic areas might be small compared with the total area; the resulting high anodic current densities would give the desirable type of corrosion, but the pits would be scattered rather than be uniformly distributed over the metal surface. Of course, if the nickel were applied as a continuous layer, such as is deposited by electroplating, then there would be no exposed iron and galvanic action could not occur. Poor adherence might be expected under these conditions and the experiment made with specimens plated by the electroless nickel process has shown that such is the case.

The effect of the nickel dip in reducing fishscaling tendencies is believed to be associated with the increase in adherence that accompanies the nickel treatment. It is also possible that the presence of the thin nickel layer inhibits fishscaling by reducing the intake of hydrogen into the steel during the firing operation. The hydrogen originates from the reaction between the dissolved water in the coating and the hot iron base (ref. 11). It was shown by Moore and Mason (ref. 12) that such a reaction does not occur when the underlying metal is nickel rather than iron.

Inasmuch as no copperheads were observed under any of the selected test conditions, the effect of the nickel dip in reducing copperheads could not be studied in the present investigation.

CONCLUSIONS

The following conclusions appear to be justified in the case of a single-frit ground-coat enamel, both with and without cobalt oxide, when applied to enameling iron and to a titanium-bearing low-carbon steel.

1. The nickel dip produced a large improvement in adherence index with specimens fired for short times, but the effect of the nickel on adherence decreased markedly as the firing time was increased.
2. Under most conditions, the nickel dip produced a larger increase in adherence index in the case of a titanium-bearing low-carbon steel than in the case of enameling iron.
3. An optimum weight of nickel deposit was found for the development of maximum adherence index for the titanium-bearing steel. This optimum varied from 50 to about 120 milligrams per square foot depending on the type of cleaning used and the type of enamel applied. Similar determinations were not made in the case of the enameling iron.
4. The nickel dip had a beneficial effect in reducing fishscaling.
5. Nickel dipping of the steel prior to enameling brought about a surface roughening during the firing operation. A relationship was noted between the degree of roughening and the measured adherence index.
6. The function of the nickel dip in improving adherence is believed to be associated with galvanic attack. The nickel apparently deposits from the aqueous solution selectively on more cathodic areas of the steel surface, thus forming local galvanic cells that begin to function immediately after the enamel fuses and wets the metal surface. During firing

the iron members of the cells corrode while the nickel areas are cathodically protected. The result is that the surface becomes roughened and the coating appears to anchor itself to the undercut surface.

National Bureau of Standards,
Washington, D. C., July 20, 1953.

REFERENCES

1. Wainer, E., and Baldwin, W. J.: Nickel Flashing and Its Relation to Enamel Adherence. Jour. Am. Ceramic Soc., vol. 28, no. 11, Nov. 1, 1945, pp. 317-326.
2. Kautz, Karl: The Effect of Iron Surface Preparation Upon Enamel Adherence. Jour. Am. Ceramic Soc., vol. 20, no. 9, Sept. 1937, pp. 288-295.
3. Moore, D. B., Pitts, J. W., Richmond, J. C., and Harrison, W. N.: The Galvanic Corrosion Theory for Adherence of Porcelain-Enamel Ground Coats to Steel. NACA TN 2935, 1953.
4. Harrison, W. N., and Sweo, B. J.: Some Fusion Properties of Ground Coat Enamels as Influenced by Composition. Res. Paper RP524, Jour. Res., Nat. Bur. Standards, vol. 10, no. 2, Feb. 1933, pp. 189-209.
5. Anon: Test for Adherence of Porcelain Enamel to Sheet Metal, a Tentative Standard Test of the Porcelain Enamel Institute. Bull. T-17, Porcelain Enamel Inst., Inc., Washington, D. C., 1951.
6. Ikenberry, I. C., and Canfield, J. J.: Rapid Method for Determining Nickel on the Surface of Enameling Iron. Jour. Am. Ceramic Soc., vol. 32, no. 10, Oct. 1, 1949, pp. 308-312.
7. Clawson, C. D.: A Study of Adherence of Ground Coats to Sheet Steel. Ceramic Ind., vol. 13, no. 2, Aug. 1929, pp. 164-166.
8. Hansen, J. E., and Irwin, J. T.: The Use of a Nickel Dip in Enameling Practice. Jour. Am. Ceramic Soc., vol. 18, no. 8, Aug. 1935, pp. 225-229.
9. Pettyjohn, James: Nickel Dip Treatment of Enameling Iron. Proc. Second Annual Porcelain Enamel Inst. Forum, 1937, pp. 56-59.
10. Higgins, W. W.: Fishscaling. Proc. Sixth Annual Porcelain Enamel Inst. Forum, 1941, pp. 71-96.
11. Moore, D. G., and Mason, M. A.: Investigation of Gases Evolved During Firing of Vitreous Coatings on Steel. NACA TN 2865, 1953. Also Jour. Am. Ceramic Soc., vol. 36, no. 8, Aug. 1953, pp. 241-249.
12. Moore, Dwight G., Mason, Mary A., and Harrison, William N.: Relative Importance of Various Sources of Defect-Producing Hydrogen Introduced Into Steel During Application of Vitreous Coatings. NACA Rep. 1120, 1953. Also Jour. Am. Ceramic Soc., vol. 35, no. 2, Feb. 1, 1952, pp. 33-41.

13. Brenner, Abner, and Riddell, Grace: Deposition of Nickel and Cobalt by Chemical Reduction. Res. Paper RPl835, Jour. Res., Nat. Bur. Standards, vol. 39, no. 5, Nov. 1947, pp. 385-395.
14. Richmond, J. C., Moore, D. G., Kirkpatrick, H. B., and Harrison, W. N.: Relation Between Roughness of Interface and Adherence of Porcelain Enamel to Steel. NACA TN 2934, 1953.
15. Dietzel, A.: Adherence in Sheet-Iron Enamelware. Sprechsaal Keramik, vol. 68, no. 1, 1935, pp. 3-6; no. 2, 1935, pp. 20-23; no. 3, 1935, pp. 34-36; no. 4, 1935, pp. 53-56; no. 5, 1935, pp. 67-99; no. 6, 1935, pp. 84-85.
16. Harrison, William N., Richmond, Joseph C., Pitts, Joseph W., and Benner, Stanley G.: Migration of Cobalt During Firing of Ground-Coat Enamels. NACA TN 2695, 1952. Also, Radioisotope Study of Cobalt in Porcelain Enamel. Jour. Am. Ceramic Soc., vol. 35, no. 5, May 1952, pp. 113-120.
17. Patrick, H. F., Porst, E. G., and Spencer-Strong, G. H.: Study of Some Phenomena Associated With the Adherence of Sheet Iron Ground Coats. Jour. Am. Ceramic Soc., vol. 36, no. 9, Sept. 1, 1953, pp. 305-313.
18. Lyman, Taylor, ed.: Metals Handbook. A.S.M. (Cleveland), 1948.
19. Gibbs, M. B., and Porter, F. R.: Properties of Steels for Porcelain Enameling. Proc. Fourteenth Annual Porcelain Enamel Inst. Forum, 1952, pp. 49-59.

TABLE 1.- COMPOSITION OF ENAMELING IRON AND
TITANIUM-BEARING LOW-CARBON STEEL

Steel	Description	Source of analysis	Element, percent by weight				
			Carbon	Phos- phorus	Sulfur	Manganese	Titanium
A	Enameling iron	Ref. 18	0.012	0.005	0.025	0.017	----
B	Titanium- bearing steel	Ref. 19	.05	.010	.030	.30	0.30

TABLE 2.- MILL BATCHES AND MILLING DATA FOR COATINGS E-1 AND E-3

[Milling fineness, 6 to 8 percent retained on a No. 200
U. S. Standard sieve; application thickness, 4 to
6 mils (fired)]

Mill batch	Parts by weight in -	
	Coating E-1	Coating E-3
Frit 109-0	100	---
Frit 109-4	---	100
Enameling clay	6	6
Borax	1	1
Water	42.5	42.5

TABLE 3.- BATCH AND COMPUTED OXIDE COMPOSITIONS OF FRIT ^a109-0

Batch composition		Computed chemical composition	
Material	Parts by weight	Component	Percent by weight
Potash feldspar	30.8	SiO ₂	51.0
Borax (hydrated)	44.3	B ₂ O ₃	16.1
Flint (silica)	30.5	Al ₂ O ₃	5.7
Sodium carbonate	9.2	Na ₂ O	15.4
Sodium nitrate	5.1	K ₂ O	3.5
Fluorspar	8.3	CaF ₂	8.3
	----		----
	128.2		100.0

^aComposition of frit 109-4 same as that of frit 109-0 except th frit 109-4 contains an addition of 0.4 percent by weight of Co₃O₄.

TABLE 4- CONCENTRATIONS OF PICKLING AND NICKEL-DIP SOLUTIONS,
SELECTED OPERATING TEMPERATURES, AND TIMES OF
IMMERSION OF STEEL SPECIMENS

Solution	Concentration, percent by weight	Bath temperature, °F	Immersion time, min
Sulfuric-acid pickle	7	150	15
Nitric-acid pickle	8	85	3
Nickel dip ^a	^b 2.25	155	6

^aPrepared by dissolving 3 oz of nickelous ammonium sulfate in one gal of water and adjusting pH to 3.0 with sulfuric acid.

^bExpressed as weight percent $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

TABLE 5.- ADHERENCE INDICES FOR GROUND-COAT ENAMEL WITH NO ADHERENCE
OXIDES (COATING E-1) ON TWO STEELS AFTER VARIOUS SURFACE
PRETREATMENTS AND AFTER VARIOUS FIRING TIMES AT 1,550° F

Type of steel (a)	Surface pretreatment (b)	Adherence index after firing at 1,550° F for - (c,d)				
		2 min	4 min	7 min	10 min	16 min
A	H ₂ SO ₄ , no nickel	4.2(L)	3.0(L)	3.6(L)	3.6(L)	3.6
B	H ₂ SO ₄ , no nickel	3.6	2.4	.6	1.8	1.2
A	H ₂ SO ₄ , nickel dip	18.2(S)	7.9(S)	9.1(S)	6.1	6.1
B	H ₂ SO ₄ , nickel dip	76.4	40.0	21.2	13.3	7.9
A	HNO ₃ , no nickel	6.1(S)	6.1(S)	7.3(S)	7.3	5.6
B	HNO ₃ , no nickel	.6	1.2	1.2	1.2	2.4
A	HNO ₃ , nickel dip	44.8(S)	43.0	20.0	18.2	8.5
B	HNO ₃ , nickel dip	85.5	73.3	55.1	29.6	17.6
A	Sandblast, no nickel	21.2(S)	19.4(L)	15.2	14.5	14.5
B	Sandblast, no nickel	24.8	21.8	19.3	13.9	10.3
A	Sandblast, nickel dip	61.2	61.8	50.3	47.8	39.4
B	Sandblast, nickel dip	73.3	49.7	52.2	51.5	40.6

^aA, enameling iron; B, titanium-stabilized low-carbon steel.

^bSee table 4 for pickling and nickel-dip treatments. Sandblasting was done at an air pressure of 80 psi with sand sized to pass a No. 20 and be retained on a No. 100 U. S. Standard sieve.

^cValues listed are averages of two specimens applied at a fired thickness of from 4.0 to 6.0 mils.

^dLetter L following an adherence-index value designates that coating had separated from metal over large areas of specimens immediately after firing. These areas, referred to as lifts, are believed to be caused by hydrogen diffusing from steel to coating-metal interface. Letter S indicates presence of small lifted areas. Where no letter follows adherence index, no lifts were noted on the specimens.

TABLE 6.- ADHERENCE INDICES FOR GROUND-COAT ENAMEL WITH 0.4 PERCENT COBALT (COATING E-3) ON TWO STEELS AFTER VARIOUS SURFACE PRETREATMENTS AND AFTER VARIOUS FIRING TIMES AT 1,550° F

Type of steel (a)	Surface pretreatment (b)	Adherence index after firing at 1,550° F for time indicated (c,d)				
		2 min	4 min	7 min	10 min	16 min
A	H ₂ SO ₄ , no nickel	t25.7(F)	57.9(F)	58.6(F)	61.0(F)	61.6
B	H ₂ SO ₄ , no nickel	11.6	49.1	61.6	64.5	71.5
A	H ₂ SO ₄ , nickel dip	t57.9(F)	62.4(f)	59.4(f)	53.9	61.2
B	H ₂ SO ₄ , nickel dip	87.5	74.5	75.8	81.3	86.1
A	HNO ₃ , no nickel	t39.8(F)	65.1(F)	66.5(f)	66.1	70.6
B	HNO ₃ , no nickel	8.7	42.1	66.3	75.9	76.8
A	HNO ₃ , nickel dip	73.9	71.7	72.1	74.3	74.0
B	HNO ₃ , nickel dip	83.0	77.8	83.4	72.4	79.9
A	Sandblast, no nickel	70.6	71.5	70.1	69.9	69.1
B	Sandblast, no nickel	61.3	81.2	75.7	75.9	76.5
A	Sandblast, nickel dip	73.4	71.3	69.2	69.7	70.9
B	Sandblast, nickel dip	82.7	66.9	68.3	70.4	60.1

^aA, enameling iron; B, titanium-stabilized low-carbon steel.

^bSee table 4 for pickling and nickel-dip treatments. Sandblasting was done with sand that was sized so as to pass a No. 20 and be retained on a No. 100 U. S. Standard sieve at an air pressure of 80 psi.

^cValues listed are averages of seven specimens, applied at a fired thickness of between 4.0 and 6.0 mils.

^dSmall letter t preceding an adherence index value indicates that a trace of fishscaling was detected 24 hr after firing. Letter F following an index value designates pronounced fishscaling of coating after heating coated specimens for 48 hr in air at 260° F; similarly, letter f indicates that a trace of fishscaling was detected. Where no letter accompanies the adherence index, no fishscaling was noted.

TABLE 7.- GAIN IN WEIGHT ON FIRING FOR 2 MINUTES AT 1,550° F
OF 4- BY 4-INCH SPECIMENS OF TWO STEELS OF VARIOUS
THICKNESSES AFTER DIFFERENT SURFACE TREATMENTS

Surface treatment (a)	Steel A		Steel B	
	Metal thickness, in.	Gain in weight, mg/sq cm (b)	Metal thickness, in.	Gain in weight, mg/sq cm (b)
P	0.018	4.70	0.025	3.53
P + N	.018	4.45	.025	2.95
S	.018	1.07	.025	.86
P	0.023	4.26	0.028	2.64
P + N	.023	4.12	.028	2.06
S	.023	.93	.028	.76
P	0.038	3.56	^c 0.049	1.96
P + N	.038	3.53	^c 0.049	1.70
S	.038	1.01	^c 0.049	.84
P	0.049	2.90	^d 0.049	2.34
P + N	.049	2.88	^d 0.049	2.28
S	.049	.94	^d 0.049	.95
P	0.057	2.47	0.051	2.38
P + N	.057	2.40	.051	1.50
S	.057	.89	.051	.77

^aP, pickled in sulfuric acid; N, nickel dip; S, sandblasted.

^bAverage of three specimens.

^cLot no. 1.

^dLot no. 2.

TABLE 8.- COMPARISON OF NICKEL ON SANDBLASTED AND NICKEL-DIPPED
SURFACES OF TITANIUM-BEARING LOW-CARBON STEEL BEFORE
AND AFTER FIRING COBALT-FREE GROUND COAT E-1 FOR
4 MINUTES AT 1,400°, 1,500°, AND 1,600° F
TOGETHER WITH ADHERENCE INDEX FOR
SAME FIRING TREATMENT

[Values are averages for two specimens]

Firing treatment		Nickel on steel		Adherence index
Time, min	Temperature, °F	Before enameling, mg/ft ²	After enameling, mg/ft ² (a)	
4	1,400	247	245	79.4
4	1,500	277	276	41.8
4	1,600	266	260	32.1

^aNickel determination was made after removal of ground coat by 5-min immersion in molten sodium hydroxide at 800° F. Ground coat was applied so that a thickness of between 3.5 and 4.0 mils was obtained after firing.

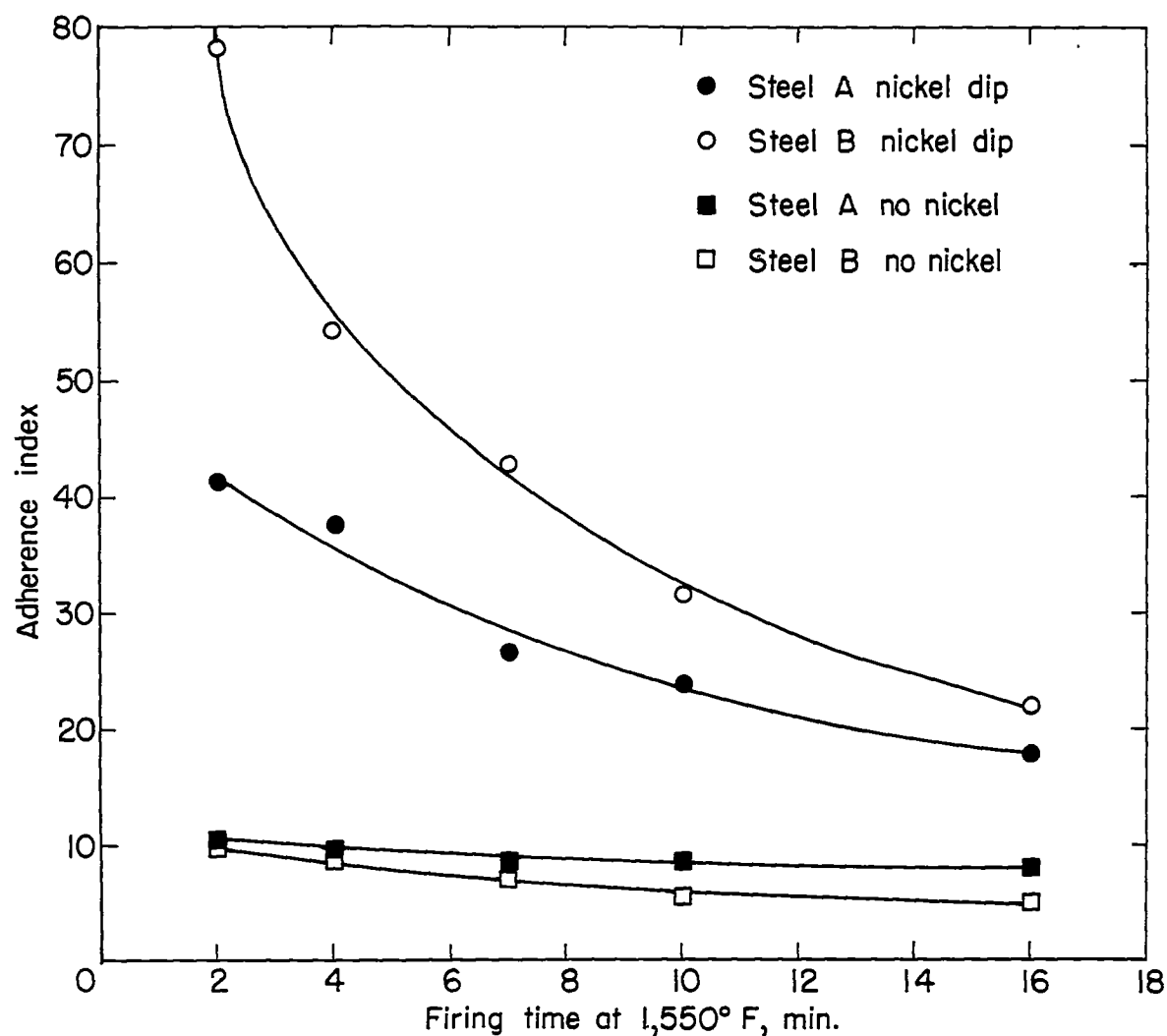


Figure 1.- Effect of firing time at 1,550° F on adherence index of cobalt-free ground coat E-1 applied to both 18-gage enameling iron (steel A) and to 18-gage titanium-bearing low carbon steel (steel B). Points are averages for specimens pickled in H_2SO_4 , specimens pickled in HNO_3 , and sandblasted specimens.

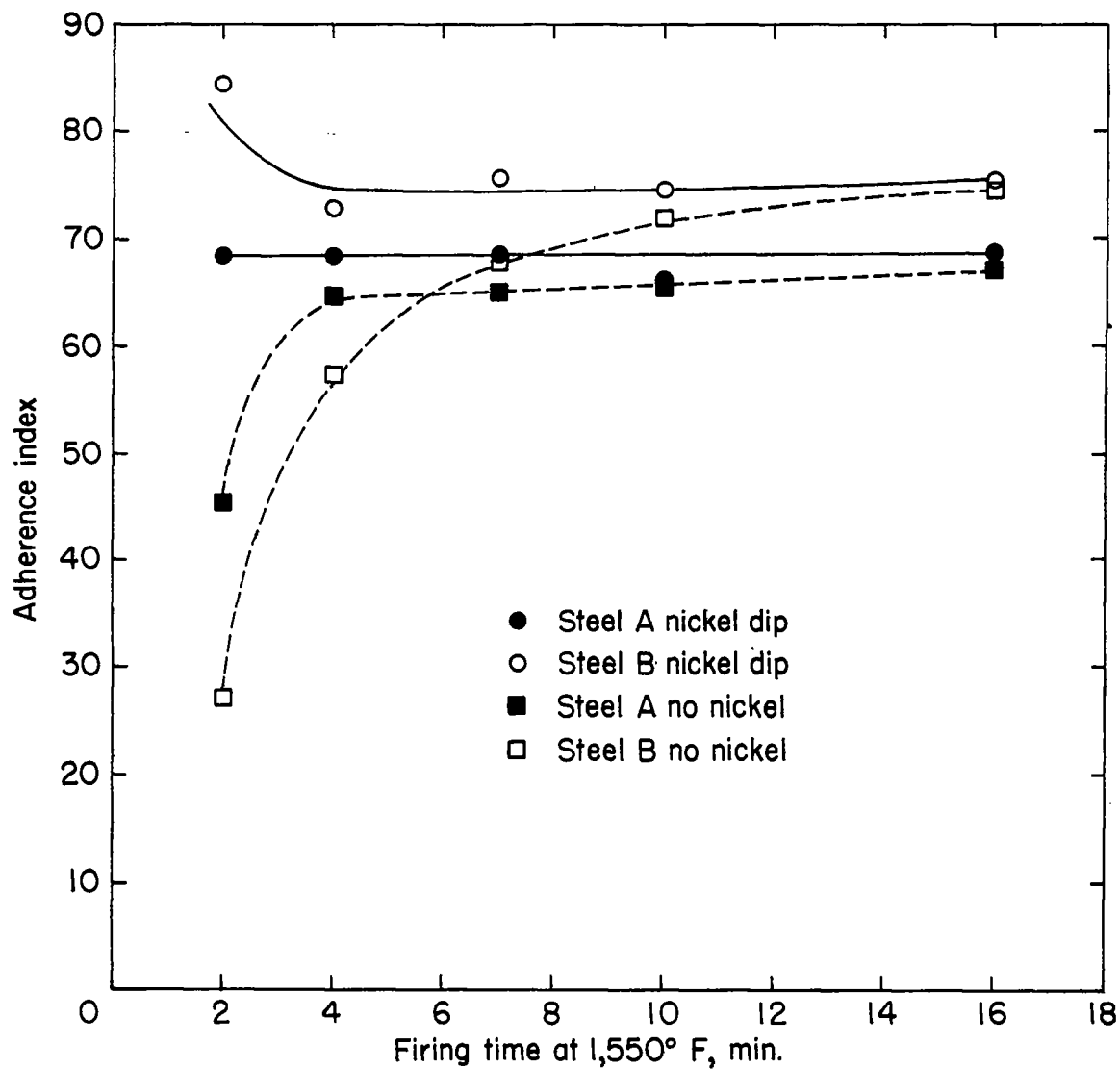


Figure 2.- Effect of firing time at 1,550° F on adherence index of cobalt-bearing ground coat E-3 applied to both 18-gage enameling iron (steel A) and to 18-gage titanium-bearing low-carbon steel (steel B). Points are averages for specimens pickled in H_2SO_4 , specimens pickled in HNO_3 , and sandblasted specimens.

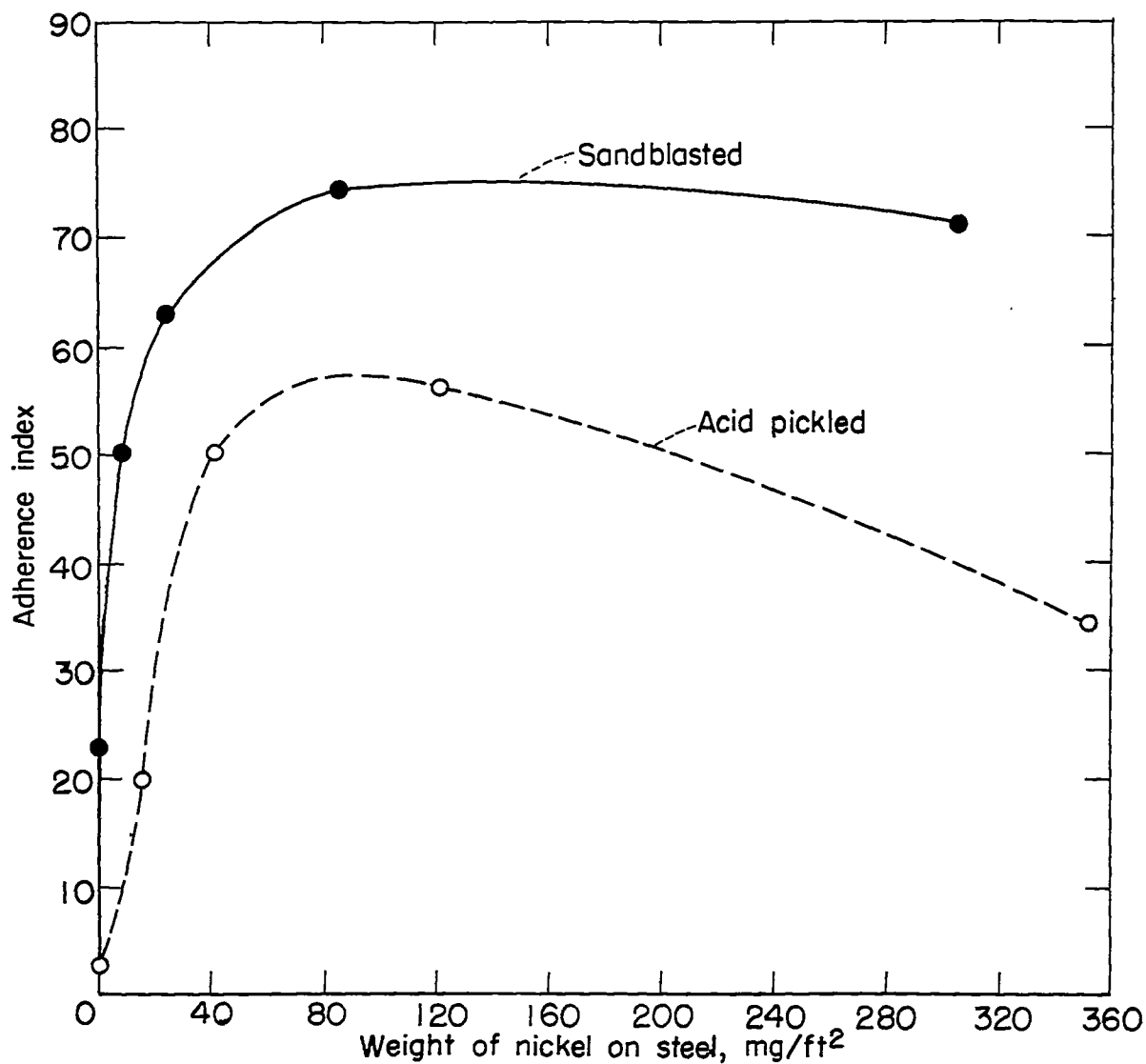


Figure 3.- Effect of weight of nickel deposit on adherence index of specimens of titanium-bearing low-carbon steel that had been coated with cobalt-free enamel E-1. Specimens were fired for 5 minutes at 1,500° F. Curve marked acid pickled is for specimens pickled in H_2SO_4 .

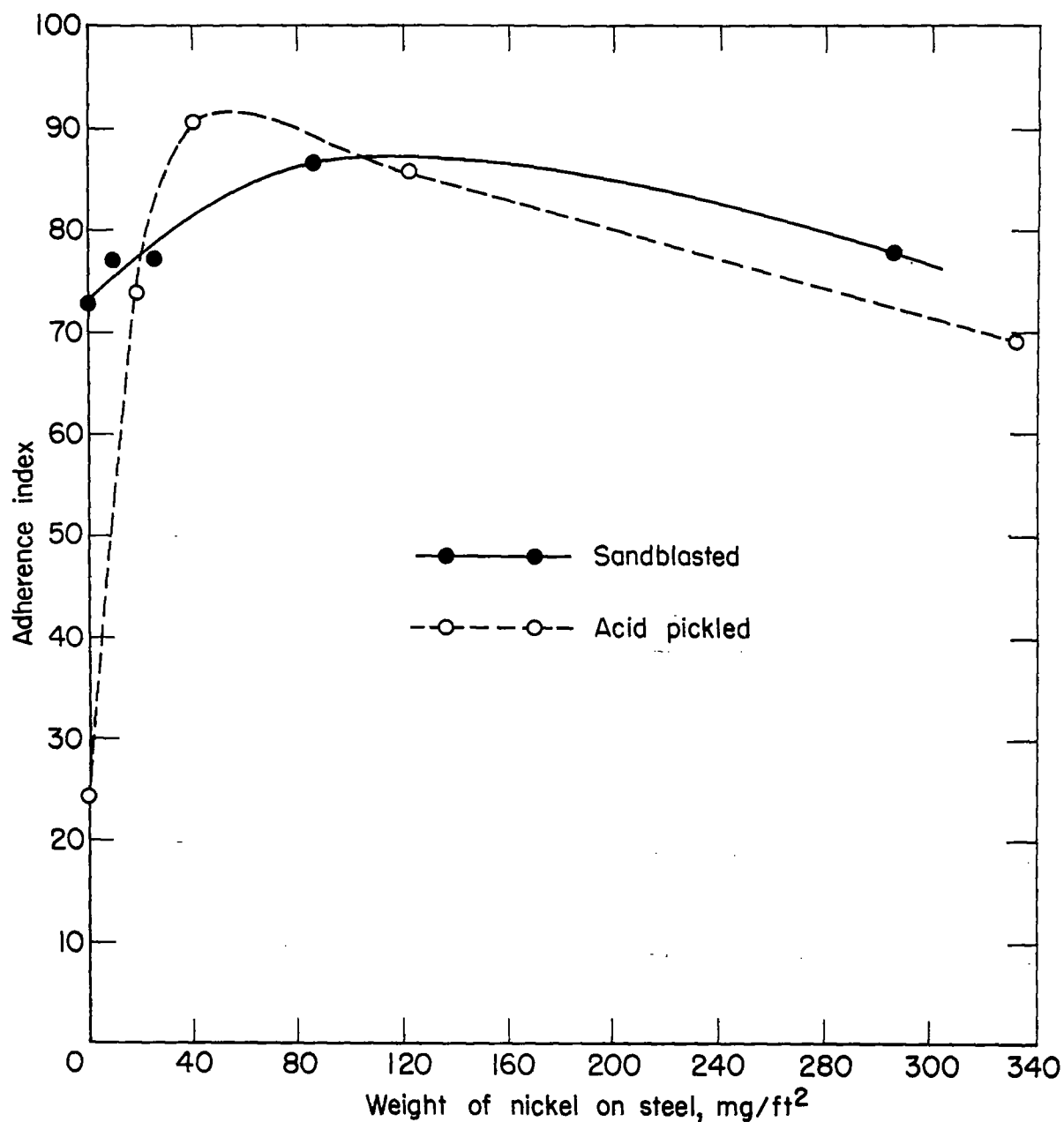


Figure 4.- Effect of weight of nickel deposit on adherence index of specimens of titanium-bearing low-carbon steel that had been coated with cobalt-bearing enamel E-3. Specimens were fired for 5 minutes at 1,500° F. Curve marked acid pickled is for specimens pickled in H_2SO_4 .



(a) Fired 2 minutes;
fishscaled.

(b) Fired 7 minutes;
fishscaled.

(c) Fired 16 minutes;
no fishscales. L-83628

Figure 5.- Photomicrographs showing differences in bubble structure of E-3 ground coat on pickled enameling iron surfaces after various firing times at 1,550° F. Bubbles attached to interface in part (c) are of a type shown previously to be caused by rapid evolution of hydrogen from steel during fast cooling. Presence of these bubbles at interface appears to prevent fishscaling. Unetched; X85.



Fired 2 min, A.I. 78



Fired 7 min, A.I. 29
(a) Nickel-dipped steel.



Fired 16 min, A.I. 7



Fired 2 min, A.I. 2



Fired 7 min, A.I. 1

(b) Steel with no nickel.



Fired 16 min, A.I. 1
L-83629

Figure 6.- Photomicrographs of interfaces between cobalt-free ground coat E-1 and titanium-bearing low-carbon steel (steel B) after various firing times at 1,550° F. Specimens were pickled in H_2SO_4 prior to coating. Note greater surface roughening on steel that had been nickel dipped and also apparent correlation between roughness of steel surface and adherence index (A.I.). Unetched; X1000.

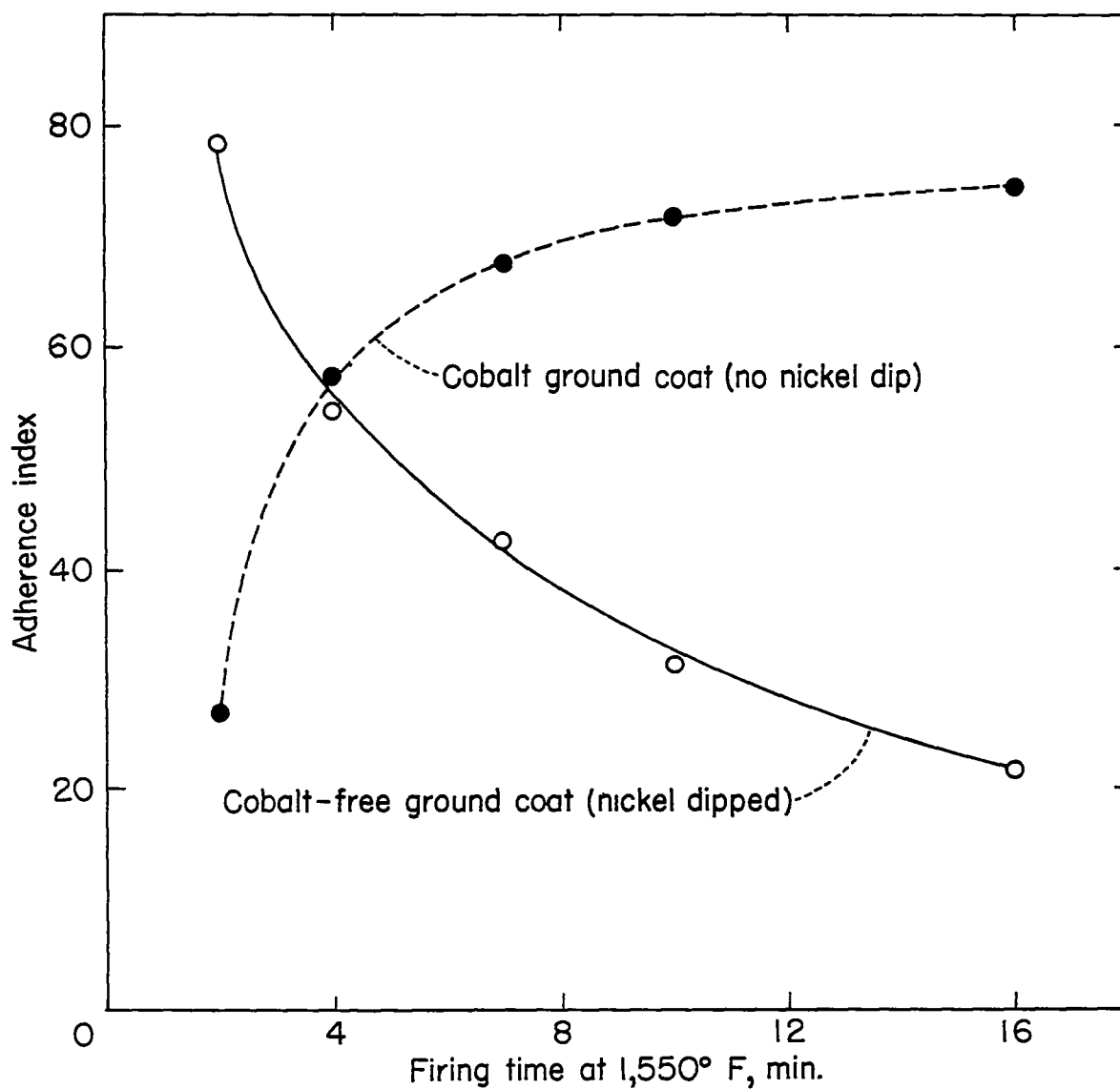


Figure 7.- Effect of firing time at 1,550° F on adherence index of cobalt-bearing ground coat E-3 applied to steel B that had not been nickel dipped compared with similar data for cobalt-free ground coat E-1 applied to nickel-dipped steel.